

666191
EP04/12108

RECEIVED

12 NOV 2004

WIPO

PCT

PA 1121256

THE UNITED STATES OF AMERICA**TO ALL TO WHOM THESE PRESENTS SHALL COME:****UNITED STATES DEPARTMENT OF COMMERCE****United States Patent and Trademark Office****February 02, 2004**

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111.**

APPLICATION NUMBER: 60/525,268**FILING DATE: November 25, 2003**

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

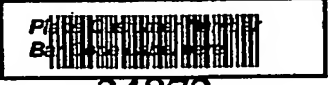
P. R. GRANT
Certifying Officer

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label N .

ER131816689US

INVENTOR(S)					
Given Name (first and middle (if any))	Family Name or Surname	Residence (City and either State or Foreign Country)			
Andrei Gernot Theo	Gonioukh Köhler Teubner	Erfstadt-Liblar, Germany Meckenheim, Germany Erfstadt, Germany			
<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
CONTINUOUS PREPARATION OF ETHYLENE HOMOPOLYMERS OR COPOLYMERS					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number		34872			
OR		Type Customer Number here		PATENT TRADEMARK OFFICE	
<input type="checkbox"/> Firm or Individual Name		William R. Reid			
Address		Basell USA Inc.			
Address		912 Appleton Road			
City		Elkton	State	MD	ZIP 21921
Country		US	Telephone	410-996-1783	Fax 410-996-1560
ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification		Number of Pages	14	<input type="checkbox"/> CD(s), Number	
<input checked="" type="checkbox"/> Drawing(s)		Number of Sheets	1	<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76					
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.				FILING FEE AMOUNT (\$)	
<input type="checkbox"/> A check or money order is enclosed to cover the filing fees					
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number.				08-2336	
<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached.				\$160.00	
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.					
<input checked="" type="checkbox"/> No.					
<input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:					

Respectfully submitted,

SIGNATURE

William R. Reid

TYPED or PRINTED NAME William R. Reid

TELEPHONE 410-996-1783

Date 11/25/2003

REGISTRATION NO.

(if appropriate)

Docket Number.

47,894

LU 6141 (US)

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

BEST AVAILABLE COPY

PROVISIONAL APPLICATION COVER SHEET
Additional Page

PTO/SB/16 (02-01)
Approved for use through 10/31/2002. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

Docket Number		LU 6141 (US)
INVENTOR(S)/APPLICANT(S)		
Given Name (first and middle (if any))	Family or Surname	Residence (City and either State or Foreign Country)
Thomas	Dröge	Diepholz, Germany

Number 2 of 2

WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

EXPRESS MAILING CERTIFICATE

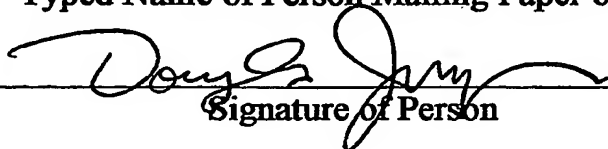
This certifies that the attached **Form PTO/SB/16** (in duplicate), **Specification (10)** for the provisional application of **Andrei Gonioukh et al.**, for **CONTINUOUS PREPARATION OF ETHYLENE HOMOPOLYMERS OR COPOLYMERS** (our ref: **LU 6141 (US)**) is being mailed by "Express Mail Post Office to Addressee" service in an envelope addressed:

Mail Stop Provisional Patent Application
Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

and deposited on **NOVEMBER 25, 2003** as "Express Mail" in the United States Postal Service, the number of the "Express Mail" mailing label being **ER131816689US**.

Douglas Jumps

Typed Name of Person Mailing Paper or Fee


Signature of Person

PATENT APPLICATION SERIAL NO. _____

U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE
FEE RECORD SHEET

12/03/2003 MEXKOHEN 00000003 082336 60525268

01 FC:1005 160.00 DA

PTO-1556
(5/87)

**CONTINUOUS PREPARATION OF ETHYLENE HOMOPOLYMERS OR
COPOLYMERS**

The present invention relates to a process for the continuous preparation of ethylene homopolymers or copolymers in the presence of free-radical polymerization initiators and, if
5 desired, molecular weight regulators at from 120°C to 350°C and pressures in the range from 100 to 4000 bar, in which the polymer is separated from unpolymerized ethylene in a high-pressure stage at a pressure of from 100 to 500 bar and at least one low-pressure stage at a pressure of from 1 to 100 bar and the ethylene separated off in the high-pressure stage is separated from remaining monomeric, oligomeric and/or polymeric constituents and recirculated
10 to the inlet of the tube reactor in a high-pressure circuit and the ethylene separated off in the low-pressure stage is separated from remaining monomeric, oligomeric and/or polymeric constituents and recirculated to the inlet of the tube reactor in a low-pressure circuit.

High pressure polymerization processes for preparing polyethylene and ethylene copolymers have been known for a long time (Ullmann's Encyclopädie der technischen Chemie,
15 4th edition, vol. 19/1980/pp.169-178). Processes carried out in high-pressure tube reactors are particularly widespread. Such processes are described, for example, in EP-A-449092, EP-A-394794, EP-B-567818 and DE-A-4102808. Here, the polymerization process is initiated by means of an initiator, for example peroxides or oxygen. The initiators are usually dissolved in an inert solvent such as isododecane (cf., for example, GB 1558883).

20 The use of relatively low-boiling paraffinic solvents for dissolving the initiators is also known. Thus, for example, US 3275615 describes the use of hexane, cyclohexane, heptane, methylcyclohexane, isooctane or other saturated hydrocarbons as solvents. FR 2362869 discloses the use of isodecane.

However, all processes known hitherto have the disadvantage that the solvent is obtained
25 in the low-pressure circuit together with other monomeric, oligomeric or polymeric constituents and therefore has to be disposed of, frequently does not meet explosion protection regulations or has an excessive adverse effect on the polyethylene product as residual solvent content or makes backventing in subsequent extrusion necessary.

It is an object of the present invention to overcome the abovementioned disadvantages of
30 the prior art and provide a process in which the solvent used for the initiators in the high-pressure polymerization of ethylene can be largely recovered in a simple fashion.

We have found that this object is achieved by the polymerization initiators being used as a solution in an isoparaffinic solvent having a boiling point of not more than 160°C and the solvent being separated from the other monomeric, oligomeric and/or polymeric constituents in the low-pressure circuit and being reused for dissolving initiator.

5 A first important factor for the success of the present invention is the use of an isoparaffinic solvent having a boiling point of not more than 160°C, preferably not more than 150°C, particularly preferably not more than 135°C, since the low boiling point makes it easier to recover the solvent according to the present invention while still ensuring high spontaneous ignition temperatures. According to the present invention, isoparaffinic solvents are all alkanes
10 which have at least one branch. Mixtures of isoparaffinic solvents or fractions of these can also be used as long as the upper end of the boiling range is below 160°C. Furthermore, it is preferred that the isoparaffinic solvent comprises isoparaffins having not more than 10 carbon atoms, preferably from 5 to 9 and particularly preferably from 6 to 8 carbon atoms.

Preferred isoparaffinic solvents are 2-methylpentane, 3-methylpentane, 2,2-
15 dimethylbutane, 2,3-dimethylbutane, 2-methylhexane, 3-methylhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, 2-methylheptane, 2,2-dimethylhexane, 2,4-dimethylhexane, 2,5 dimethylhexane, 3,4-dimethylhexane, 2,2,4-trimethylpentane (isooctane), 2-methyloctane and mixtures thereof. The solvent used is particularly preferably a mixture of isoparaffins having a boiling range from 100 to 150°C, in
20 particular from 110 to 140°C.

The recovery of the major part of the solvent makes it possible to employ even relatively expensive solvents which would otherwise not be feasible for economical operation.

The Initiators can be employed in each zone of the tube reactor, either individually or as a mixture, in concentrations of from 0.1 to 50 mol/t of polyethylene produced, in particular from
25 0.2 to 20 mol/t. The initiator mixtures are present in the solutions in proportions of from 2 to 65% by weight, preferably from 5 to 40% by weight and particularly preferably from 10 to 30% by weight. Furthermore, particular preference is given to using mixtures of initiators which have different decomposition temperatures.

A second aspect which is important for the present invention is that the solvent is
30 separated from the other monomeric, oligomeric and/or polymeric constituents in the low-pressure circuit in such a way that it is suitable for reuse as solvent for initiators.

The separation is preferably carried out by separating off the solvent in the low-pressure circuit by means of at least one first and one last gas-liquid separator which are connected in series, with the temperature being reduced from separator to separator so that the other monomeric, oligomeric or polymeric constituents are separated out in the first separator or
5 separators and the solvent being separated out as liquid essentially in the last separator. The solvent is then, if appropriate in admixture with fresh solvent, reused for dissolving initiator.

As a result of the isoparaffinic solvent being separated from ethylene and any comonomers essentially in the last separator after the other high-boiling constituents have been separated off in the upstream separator or separators, preferably at least two separators, the
10 solvent is obtained in a form which is not excessively contaminated with the other constituents. A relatively large amount of oligomeric or polymeric constituents can lead to the solvent no longer being able to be conveyed because of an excessively high viscosity, while contamination with molar mass regulators or other additives have an adverse effect on the product properties of the product on further use. The solvent is then taken from the last separator and is used again,
15 either directly or after a simple purification, for dissolving further initiators. According to the present invention, it is not necessary for the solvent which has been separated off to be purified further and preference is therefore given to using the solvent which has been separated off without further purification for dissolving initiator.

Apart from the process engineering advantages of the present invention, there are also
20 product improvements. Thus, the use of the solvent employed according to the present invention results in a lower residual solvent content in the polyethylene product, or at the same residual solvent content it is possible to omit the customary backventing in extrusion. Furthermore, the use of the isoparaffinic solvents employed according to the present invention makes it possible for part of the molar mass regulators customarily used, which are frequently also described as
25 modifiers, to be replaced by the isoparaffinic solvent. Particularly when using polar substances (aldehydes, ketones, alcohols), this has the advantage that the organoleptic properties of the polymer product are improved considerably.

For safety reasons, preference is given to using an isoparaffinic solvent having a spontaneous ignition temperature in accordance with DIN 51794 of above 250°C. Particular
30 preference is given to using an isoparaffinic solvent having a spontaneous ignition temperature of above 300°C, in particular 320°C. Furthermore, particular preference is given to isoparaffinic

hydrocarbons having a boiling point of from not less than 60°C to not more than 150°C, in particular from not less than 80°C to not more than 135°C.

It is particularly advantageous for the pressure upstream of the last separator to be increased to such an extent that the solvent condenses while the ethylene remains in the gaseous state.

The process of the present invention can be used both for the homopolymerization of ethylene and for the copolymerization of ethylene with one or more other monomers, provided that these monomers can be copolymerized with ethylene by a free-radical mechanism under high pressure. Examples of suitable copolymerizable monomers are α,β -unsaturated C₃-C₈-carboxylic acids, in particular maleic acid, fumaric acid, itaconic acid, acrylic acid, methacrylic acid and crotonic acid, derivatives of α,β -unsaturated C₃-C₈-carboxylic acids, e.g. unsaturated C₃-C₁₅-carboxylic esters, in particular esters of C₁-C₆-alkanols, or carboxylic anhydrides, in particular methyl methacrylate, ethyl methacrylate, n-butyl methacrylate or tert-butyl methacrylate, methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methacrylic anhydride, maleic anhydride or itaconic anhydride, and α -olefins such as propene, 1-butene, 1-pentene, 1-hexene, 1-octene or 1-decene. Furthermore, vinyl carboxylates, particularly preferably vinyl acetate, can also be used as comonomers. Particularly advantageous comonomers are n-butyl acrylate, acrylic acid and methacrylic acid. The proportion of comonomer or comonomers in the reaction mixture is from 0.1 to 45% by weight, preferably from 3 to 30% by weight, based on the amount of ethylene. In the copolymerization, the further monomers are preferably fed in at a plurality of points along the reactor.

Initiation of the polymerization reaction using organic peroxides or azo compounds represents a preferred embodiment of the process of the present invention. Examples of suitable organic peroxides are peroxy esters, peroxy ketals, peroxy ketones and peroxycarbonates, e.g. di(2-ethylhexyl) peroxydicarbonate, dicyclohexyl peroxydicarbonate, diacetyl peroxydicarbonate, tert-butylperoxy isopropyl carbonate, di-tert-butyl peroxide, di-tert-amyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-di-tert-butylperoxyhexane, tert-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy)hex-3-yne, 1,3-diisopropyl monohydroperoxide or tert-butyl hydroperoxide, didecanoyl peroxide, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, tert-amylperoxy 2-ethylhexanoate, dibenzoyl peroxide, tert-butylperoxy 2-ethylhexanoate, tert-butylperoxy diethylacetate, tert-butylperoxy

diethylisobutyrate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di-(tert-butylperoxy)cyclohexane, tert-butyl peroxyacetate, cumyl peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-amyl peroxy-pivalate, tert-butyl peroxyneodecanoate, tert-butyl permaleate, tert-butyl peroxy-pivalate, tert-butyl peroxyisooctanoate, diisopropylbenzene
5 hydroperoxide, cumene hydroperoxide, tert-butyl peroxybenzoate, methyl isobutyl ketone hydroperoxide, 3,6,9-triethyl-3,6,9-trimethyltriperoxycyclononane or 2,2-di(tert-butylperoxy)butane. Azoalkanes (diazenes), azodicarboxylic esters, azodicarboxylic dinitriles such as azobisisobutyronitrile and also hydrocarbons which disintegrate into radicals and are also referred to as C-C initiators, e.g. 1,2-diphenyl-1,2-dimethylethane derivatives and 1,1,2,2-
10 tetramethylethane derivatives, are also suitable. It is possible to use both individual initiators and, preferably, mixtures of various initiators. A wide range of initiators, in particular peroxides, are commercially available, for example the products sold by Akzo Nobel under the trade names Trigonox® or Perkadox®.

The polymerization is preferably carried out in a tube reactor having a plurality of
15 reaction zones, more preferably 2-6 reaction zones, particularly preferably from 3 to 5 reaction zones. The polymerization is initiated in each polymerization zone by addition of initiators which decompose to form free radicals. The tube reactor preferably has a length-to-diameter ratio of >1000.

In the process of the present invention, the molar mass of the polymers prepared can be
20 controlled in a customary fashion by addition of molecular weight regulators. Examples of suitable regulators are hydrogen, aliphatic and olefinic hydrocarbons such as propane, butane, pentane, hexane, cyclohexane, propene, 1-pentene, 1-hexene or 1-octene, ketones, such as acetone, methyl ethyl ketone (2-butanone), methyl isobutyl ketone, methyl isoamyl ketone, diethyl ketone or diamyl ketone, aldehydes such as formaldehyde, acetaldehyde or
25 propionaldehyde and saturated aliphatic alcohols such as methanol, ethanol, propanol, isopropanol or butanol. Particular preference is given to using saturated aliphatic aldehydes, in particular propionaldehyde, alkanes such as propane or α -olefins such as propene or 1-hexene. The molar mass regulator is preferably introduced into the reaction mixture upstream of the tube reactor. It can also be introduced together with the polymerization initiator at one or more points
30 along the tube reactor. An advantage of the present invention is that the isoparaffinic solvents can also partly replace the molar mass regulator.

The process of the present invention is usually carried out at pressures of from 1000 to 4000 bar, with pressures of from 1800 to 3500 bar being preferred and pressures of from 2000 to 3300 bar being particularly preferred. The temperatures are generally in a range from 100 to 350°C, preferably from 140 to 340°C and very particularly preferably from 150°C to 330°C, with the copolymerization of ethylene with sensitive or strongly regulating comonomers, in particular free-radically polymerizable carboxylic esters such as vinyl esters, preferably being carried out at below 230°C. In general, preference is given to a process in which the polymerization temperature is not higher than 330°C.

The flowing reaction mixture generally contains polyethylene in an amount in the range from 0 to 45% by weight, based on the total weight of the monomers fed into the reactor, usually up to 40% by weight.

The present invention further provides an apparatus for the high-pressure polymerization of ethylene and, if desired, comonomers, which is suitable and preferred for carrying out the process of the present invention, comprising

- a) a high-pressure tube reactor which has at least one feed point for the monomer and at least one feed point for a solution of polymerization initiators,
 - b) at least one mixing vessel for dissolving the polymerization initiators in an isoparaffinic solvent having a boiling point of not more than 160°C, which is connected to the feed point or points,
 - c) a high-pressure stage and at least one low-pressure stage for separating unpolymerized reaction constituents from the polymer product,
 - d) a high-pressure circuit for recirculating the monomer separated off in the high-pressure stage to the inlet of the tube reactor,
 - e) a low-pressure circuit for recirculating the monomer separated off in the low-pressure stage, which circuit comprises at least one first separator for separating the other reaction constituents from the monomer and solvent and a last separator for separating the solvent from the monomer, with heat exchangers being provided between the separators, and
 - f) a return line for recirculating the solvent from the last separator to the mixing vessel or vessels.
- A collection vessel in which the recovered solvent is temporarily stored is preferably provided between return line and mixing vessel.

The invention is described in more detail below with the aid of the figure without being restricted to the embodiments described.

The figure schematically shows a continuous polymerization plant for preparing ethylene homopolymers or copolymers. The ethylene, which is usually under a pressure of 17 bar, is
5 firstly compressed to a pressure of about 300 bar by means of a precompressor 3a and then compressed to the reaction pressure of about 3000 bar using an after-compressor 3b. After mixing with a suitable molar mass regulator, in this case propionaldehyde, and preheating to the reaction start temperature of from about 150 to 175°C, the reaction mixture is conveyed to the initiator feed points 12a, 12b, 12c of the tube reactor 1.

10 The tube reactor 1 comprises in principle a long tube having a length of 600 m and a diameter of 15 mm, which in the present case is divided into three reaction zones. The heat of reaction liberated is removed from the reaction mixture by means of a coolant circuit (not shown). At the beginning of each reaction zone, an individual mixture of various organic peroxides which are dissolved in an isoparaffin fraction having a boiling range from 116 to
15 134°C and a spontaneous ignition temperature above 300°C is fed into the reactor. Each mixture has a composition such that an optimum temperature profile is established in the reactor, with the maximum permissible temperature of the reaction zone not being exceeded.

At the first initiator feed point 12a of the tube reactor 1, the initiators introduced are peroxides which decompose at low temperature, e.g. tert-butyl peroxy-pivalate (TBPP), tert-amyl
20 peroxy-pivalate (TAPP), tert-butyl peroxy-neodecanoate (TBPND) or tert-amyl peroxy-neodecanoate (TAPND), one or more peroxides which decompose at intermediate temperatures, e.g. tert-butyl peroxy-2-ethylhexanoate (TBPEH), tert-butyl peroxy-3,5,5-trimethylhexanoate (TBPIN), 2,2-di(tert-butylperoxy)butane (BU-50), 1,1-di(tert-butylperoxy)cyclohexane (CH-50) and one or more peroxides which decompose at high
25 temperatures, e.g. di-tert-butyl peroxide (DTBP), tert-butyl hydroperoxide (TBHP), 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TETMTPN).

At the second initiator feed point 12b, at which the reaction temperature has dropped back to 250°C after the first temperature maximum, a mixture of one or more peroxides which decompose at intermediate temperature, e.g. tert-butyl peroxy-2-ethylhexanoate (TBPEH), tert-
30 butyl peroxy-3,5,5-trimethylhexanoate (TBPIN), 2,2-di(tert-butylperoxy)butane (BU-50), 1,1-di(tert-butylperoxy)cyclohexane (CH-50), and one or more peroxides which decompose at high

temperatures, e.g. ditert-butyl peroxide (DTBP), tert-butyl hydroperoxide (TBHP), 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TETMTPN), is added.

At the third initiator feed point 12c, at which the reaction temperature has once again dropped to below 250°C after the second temperature maximum, a mixture of one or more peroxides which decompose at intermediate temperatures, e.g. tert-butyl peroxy-2-ethylhexanoate (TBPEH), tert-butyl peroxy-3,5,5-trimethylhexanoate (TBPIN), 2,2-di(tert-butylperoxy)butane (BU-50), 1,1-di(tert-butylperoxy)cyclohexane (CH-50), and one or more peroxides which decompose at high temperatures, e.g. ditert-butyl peroxide (DTBP), tert-butyl hydroperoxide (TBHP), 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (TETMTPN), is added.

After leaving the tube reactor 1, the resulting polymer is separated off from unreacted ethylene and other low molecular weight compounds (monomers, oligomers, polymers, additives, solvent, etc) in a customar manner, by means of a high-pressure separator 4a and a low-pressure separator 4b and discharged and pelletized via an extruder 11 and granulator. In the extruder, backventing is customarily provided to reduce the residual solvent content further, but when using an isoparaffinic solvent having a boiling point of not more than 160°C this can be omitted since the solvent content is sufficiently low even without further backventing.

The ethylene which has been separated off in the high-pressure separator 4a is freed of other constituents in at least one purification stage, preferably a plurality of purification stages, in the high-pressure circuit 9 at 300 bar and fed back into the inlet end of the tube reactor 1 between precompressor 3a and after-compressor 3b.

The ethylene which has been separated off in the low-pressure separator 4b, which further comprises, inter alia, the major part of the low molecular weight products of the polymerization (oligomers) and the solvent, is worked up at a pressure of from about 1.1 to 4 bar in a plurality of separators 5a, 5b, 5c, 5d, with a heat exchanger being located between each of the separators and a compressor 3c being located between separator 5c and separator 5d. The heat exchangers 8c, 8d, 8e serve to cool the reaction mixture from separator to separator so that fractionation of the constituents according to boiling point is achieved. In the first separators 5a to 5c, the ethylene together with the major part of the solvent is separated from the other constituents, with essential oligomers and polymers being obtained in the first separator 5a and the further constituents being separated off in the separators 5b and 5c. Finally, the

ethylene/solvent mixture is compressed by means of the compressor 3c to such an extent that the solvent is removed from the ethylene at about 40°C and 5 bar in the separator 5d. After a further compression stage 3d, the ethylene is fed to the suction side of the precompressor 3a.

5 The solvent recovered in the separator 5d is sufficiently pure for it to be able to be used together with fresh solvent for dissolving further initiator. It is conveyed via a return line 14 to a stock vessel and from there fed together with fresh solvent to the mixing vessels 13a, 13b, 13c and reused for dissolving the corresponding initiator mixture.

Examples

Example 1

10 Using the polymerization plant described with reference to the figure, ethylene polymers having different densities and MFR were prepared using propionaldehyde (PA) as molar mass regulator. As solvents for the peroxide initiator mixtures, use was made of an isoparaffin fraction having a boiling range from 116 to 134°C (IP). The recovered solvent was used in a 1:1 mixture with fresh solvent for the dissolution of the peroxide initiator mixtures. The solvent
15 contained small amounts of low molecular weight polymerization products as impurities, but these did not adversely affect reuse.

Comparative Example A

Comparative Example A was carried out under conditions identical to those in Example 1, but isododecane (IDD) was used instead of the low-boiling isoparaffin mixture as solvent for
20 the peroxides.

The melt flow rate (MFR) of the resulting polymers was measured at 190°C under a load of 2.16 kg in accordance with ISO 1133. The density was determined in accordance with ISO 1183.

25 The distribution of the solvent over the separators 5b, 5c and 5d in Example 1 and Comparative Example A, can be seen in Tabelle 2. While in Example 1 the isooctane is obtained virtually exclusively in separator 5d, the isododecane is distributed over the three separators 5b, 5c and 5d and is additionally mixed with the molar mass regulator and waxes. The proportion of molar mass regulators is so high that the solvent is not suitable for the dissolution of initiator without prior purification. Furthermore, the waxes present in the solvent
30 greatly reduce the flowability on compression.

Table 1								
Example	Polymer density	MFR	Con-version	Solvent used			Molar mass regulator	
				Type	Amount of fresh solvent	Amount of recycled solvent	Type	Amount
	g/cm³	g/10min	%		kg/t of PE	kg/t of PE		kg/t of PE
1	0.9240	0.8	25.9	IP	8.2	8.2	PA	0.8
A	Polymerization not possible*			IDD	7.5	7.5	PA	

* Initiator solution was not able to be pumped

Table 2: Distribution of the solvent over the separators			
		Comp. Example	Example 1
Separator 5b	Amount separated off, 1/24h	101.6	1.3
	Solvent, % by weight	97.5	67.0
	Modifier, % by weight	2.5	33.0
Separator 5c	Amount separated off, 1/24h	133.4	4.1
	Solvent, % by weight	98.8	87.0
	Modifier, % by weight	1.2	13.0
Separator 5d	Amount separated off, 1/24h	65.0	292.4
	Solvent, % by weight	99.3	97.3
	Modifier, % by weight	0.7	2.7

List of reference numerals

	1	Tube reactor
	2	Preheater
	3a	Precompressor
5	3b	After-compressor
	3c,3d	Compressors
	4a	High-pressure separator
	4b	Low-pressure separator
	5a-5d	Separators
10	6	Pressure maintenance valve (pressure-actuated valve)
	7	Product valve
	8a-8f	Heat exchangers
	9	High-pressure circuit
	10	Low-pressure circuit
15	11	Extruder
	12a-12c	Feed points
	13a-13c	Mixing vessels
	14	Return line
	15	Stock vessel

We claim:

1. A process for the continuous preparation of ethylene homopolymers or copolymers in the presence of free-radical polymerization initiators and, if desired, molecular weight regulators at from 120°C to 350°C and pressures in the range from 100 to 4000 bar, in which the polymer is separated from unpolymerized ethylene and if appropriate from comonomers in a high-pressure stage (4a) at a pressure of from 100 to 500 bar and at least one low-pressure stage (4b) at a pressure of from 1 to 100 bar and the ethylene separated off in the high-pressure stage (4a) is separated from remaining monomeric, oligomeric and/or polymeric constituents and recirculated to the inlet of the tube reactor in a high-pressure circuit (9) and the ethylene separated off in the low-pressure stage (4b) is separated from remaining monomeric, oligomeric and/or polymeric constituents and recirculated to the inlet of the tube reactor in a low-pressure circuit (10), wherein the polymerization initiator is used as a solution in an isoparaffinic solvent having a boiling point of not more than 160°C and the solvent is separated from the other monomeric, oligomeric and/or polymeric constituents in the low-pressure circuit (10) and is reused for dissolving initiator.
2. A process as claimed in claim 1, wherein the solvent is separated off in the low-pressure circuit (10) by means of at least a first gas-liquid separator and a last gas-liquid separator connected in series (5a, 5b, 5c, 5d), with the temperature being reduced from separator to separator so that the other monomeric, oligomeric or polymeric constituents are separated out in the first separator or separators (5a, 5b, 5c) and the solvent is separated out as liquid essentially in the last separator (5d).
3. A process as claimed in claim 1 or 2, wherein the isoparaffinic solvent has a boiling point of not more than 150°C, preferably not more than 135°C.
4. A process as claimed in any of the preceding claims, wherein the solvent which has been separated off is used without further purification for dissolving initiator.
5. A process as claimed in any of claims 2 to 4, wherein the pressure upstream of the last separator is increased to such an extent that the solvent condenses while the ethylene is present in gaseous form.

6. A process as claimed in any of the preceding claims, wherein the isoparaffinic solvent has a spontaneous ignition temperature in accordance with DIN 51794 of at least 250°C, in particular at least 300°C.
7. A process as claimed in any of the preceding claims, wherein the solvent used is a mixture of isoparaffins having a boiling range from 100 to 150°C, in particular from 110 to 140°C.
8. An apparatus for the high-pressure polymerization of ethylene and, if desired, comonomers, comprising
 - a) a high-pressure tube reactor (1) which has at least one feed point for the monomer and at least one feed point (12a, 12b, 12c) for a solution of polymerization initiators,
 - b) at least one mixing vessel (13a, 13b, 13c) for dissolving the polymerization initiators in an isoparaffinic solvent having a boiling point of not more than 160°C, which is connected to the feed point or points (12a, 12b, 12c),
 - c) a high-pressure stage (4a) and at least one low-pressure stage (4b) for separating unpolymerized reaction constituents from the polymer product,
 - d) a high-pressure circuit (9) for recirculating the monomer separated off in the high-pressure stage (4a) to the inlet of the tube reactor (1),
 - e) a low-pressure circuit (10) for recirculating the monomer separated off in the low-pressure stage (4b), which circuit comprises at least one first separator (5a, 5b, 5c) for separating the other reaction constituents from the monomer and solvent and a last separator (5d) for separating the solvent from the monomer, with heat exchangers (8c, 8d, 8e) being provided between the separators (5a, 5b, 5c, 5d), and
 - f) a return line (14) for recirculating the solvent from the last separator (5d) to the mixing vessel or vessels (13).
9. An apparatus as claimed in claim 5, wherein a collection vessel is provided between return line (14) and mixing vessel(s) (13a, 13b, 13c).

Abstract

The invention relates to a process for the continuous preparation of ethylene homopolymers or copolymers in the presence of free-radical polymerization initiators and, if desired, molecular weight regulators at from 120°C to 350°C and pressures in the range from 100 to 4000 bar, in which the polymer is separated from unpolymerized ethylene in a high-pressure stage at a pressure of from 100 to 500 bar and at least one low-pressure stage at a pressure of from 1 to 100 bar and the ethylene separated off in the high-pressure stage is separated from remaining monomeric, oligomeric and/or polymeric constituents and recirculated to the inlet of the tube reactor in a high-pressure circuit and the ethylene separated off in the low-pressure stage is separated from remaining monomeric, oligomeric and/or polymeric constituents and recirculated to the inlet of the tube reactor in a low-pressure circuit. The initiator is used as a solution in an isoparaffinic solvent having a boiling point of not more than 160°C and the solvent is separated from the other monomeric, oligomeric and/or polymeric constituents in the low-pressure circuit. The solvent is then, if appropriate after being admixed with fresh solvent, reused for dissolving initiator.

Fig.

